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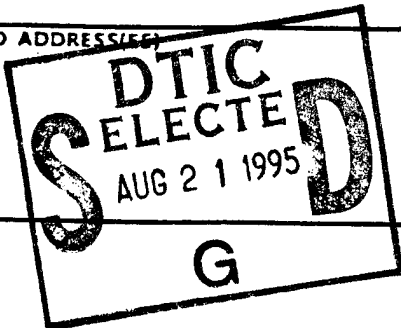
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13. ABSTRACT (Maximum 200 words)
The objective of this project was to develop new chemistry that could be applied to an efficient fuel cell operating directly on organic fuels under ambient or near-ambient conditions. The report summarizes scientific accomplishments, including the discoveries that a) soluble metal complexes offer potential advantages over traditional metal surfaces for hydrocarbon oxidation, although simultaneously optimizing the rate and potential for such oxidations (as is needed for fuel cell application) is a significant challenge that has not yet been solved; b) direct four-electron reduction of O₂ has been achieved by a catalyst capable of multiple electron transfer; and c) a new liquid feed fuel cell that operates directly on organic fuels such as methanol, and that includes a superacidic surfactant as an important component, has achieved levels of performance that significantly improve on previous work. Also included are bibliographic information for approximately 60 publications, presentations and patents resulting from work under this grant.
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OFFICE OF NAVAL RESEARCH
FINAL REPORT
FUNDAMENTAL STUDIES ON C-H ACTIVATION
FOR ALKANE FUEL CELL APPLICATIONS

Principal Investigator: Harry B. Gray

Part I: Objective, Approaches and Scientific Conclusions

The objective of this project was to develop new chemistry that could be applied to an efficient fuel cell operating directly on organic fuels under ambient or near-ambient conditions. The work was carried out primarily at the California Institute of Technology and the University of Southern California (with collaborations with the Jet Propulsion Laboratory and a number of other institutions supported under related programs). The approaches followed here included: designing, synthesizing and testing soluble (metal complex) catalysts for the oxidation of hydrocarbon fuels under mild conditions, and carrying out mechanistic and related studies on the chemistry of these catalysts in order to understand and improve their potential performance in the anode of a hydrocarbon-based fuel cell; designing multi-electron transfer complexes as catalysts for the direct four-electron reduction of dioxygen, leading to improved cathodic performance in an oxygen-based fuel cell; and investigating the potential power of superacidic electrolytes to improve fuel cell performance. Among the scientific conclusions (see the Publications below for a more complete accounting), it has been determined that a) soluble metal complexes do offer potential advantages over traditional metal surfaces for hydrocarbon oxidation, although simultaneously optimizing the rate and potential for such oxidations (as is needed for fuel cell application) is a significant challenge that has not yet been solved; b) direct four-electron reduction of O₂ has been achieved by a catalyst capable of multiple electron transfer; and c) a new liquid feed fuel cell that operates directly on organic fuels such as methanol, and that includes a superacidic surfactant as an important component, has achieved levels of performance that significantly improve on previous work.

Part II: Research Associates

The following is a list of undergraduate and graduate students, and post-doctoral fellows, funded through the grant, identified as being at Caltech (CIT) or University of Southern California (USC)

Undergraduate Students:

S. Abedin, M. Carlson, R. Hunter, R. Jarosiewicz, E. Wasinger (all CIT)

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J. Bailey (CIT), P. Batamack (USC), D. Conrad (CIT), D. Deffieux (USC), E. Fowles (CIT), M. Freund (CIT), A. Herring (CIT), M. Hill (CIT), C. Kang (CIT), R. Knieler (USC), C. Lambert (USC), I. Lauermann (CIT), Y. Lei (CIT), S. Li (CIT), D. Lyon (CIT), G. Luinstra (CIT), M. Minas da Piedad (CIT), R. Pichika (USC), G. Rasul (USC), C. Rong (CIT), E. Sabatani (CIT), C. Shi (CIT), B. Steiger (CIT), G. Stolp (USC), A. Sykes (CIT), N. Trivedi (USC), L. Wang (CIT), Q. Wang (USC), J. Zhang (CIT)

Part III: Publications, Presentations, Patents and Awards

Publications:

1. D. C. Smith and H. B. Gray, "Catalysis of the Oxidation of 1,4-Cyclohexadiene to Benzene by Electroactive Binuclear Rhodium Complexes," *Catal. Lett.* **1990**, *6*, 195.
2. K. K. Irikura and J. L. Beauchamp, "Gas-Phase Synthesis of Metalloporphyrin Ions," *J. Am. Chem. Soc.* **1991**, *113*, 2767.
3. K. K. Irikura and J. L. Beauchamp, "Methane Oligomerization in the Gas Phase by Third-Row Transition Metal Ions," *J. Am. Chem. Soc.* **1991**, *113*, 2769.
4. J. A. Labinger, "Mechanism-Imposed Limitations on the Yield of Higher Hydrocarbons from the Oxidative Coupling of Methane, and Alternate Approaches to Methane Conversion," *Preprints, ACS Div. Petr. Chem.* **1991**, *36*, 151.
5. E. H. Fowles, J. A. Labinger, J. L. Beauchamp and B. Fultz, "Fast Ion Conductors as Oxidation Catalysts: Oxidative Coupling and Deep Oxidation of Methane over Transition Metal Exchanged β -Alumina," *J. Phys. Chem.*, **1991**, *95*, 7393.
6. K. K. Irikura and J. L. Beauchamp, "Electronic Structure Considerations for Methane Activation by Third-Row Transition Metal Ions," *J. Phys. Chem.* **1991**, *95*, 8344.
7. R. A. Newman, D. S. Martin, R. F. Dallinger, W. H. Woodruff, A. Eaefer, V. M. Miskowski and H. B. Gray, "Vibrational and Electronic Spectra of $[\text{Pt}_2(\text{SO}_4)_4]^{2-}$ Complexes," *Inorg. Chem.* **1991**, *30*, 4647.
8. K.-K. Shiu and F. C. Anson, "Attempts to Immobilize Catalytically Active Heteropolytungstates on the Surfaces of Electrodes," *J. Electroanal. Chem.*, **1991**, *309*, 115.

9. C. Shi and F. C. Anson, "Multiple Intramolecular Electron-Transfer in the Catalysis of the Reduction of Dioxygen by Cobalt *meso*-Tetrakis(4-pyridyl)porphyrin to Which Four Ru(NH₃)₅ Groups Are Coordinated," *J. Am. Chem. Soc.*, **1991**, *113*, 9564.

10. J. A. Labinger, A. M. Herring and J. E. Bercaw, "Selective Hydroxylation of Hydrocarbons by Platinum Salts in Aqueous Medium. Direct Conversion of Ethanol to Ethylene Glycol," *ACS Symposium Series*, **1992**, *230*, 221.

11. J. A. Labinger, "Overcoming the Problem of Selectivity in Methane Activation via Homogeneous Catalysis," *Preprints, ACS Div. Petr. Chem.* **1992**, *37*, 289.

12. W. P. Schaefer, D. K. Lyon, J. A. Labinger and J. E. Bercaw, "A Platinum Chloro, (Fluoroaryl)Phosphine Complex," *Acta Cryst.*, **1992**, *C48*, 1582.

13. R. E. Marsh, W. P. Schaefer, D. K. Lyon, J. A. Labinger and J. E. Bercaw, "Structure of Trimethylplatinum(IV) with a Tripod Ligand," *Acta Cryst.*, **1992**, *C48*, 1603.

14. J. A. Bailey and H. B. Gray, "A μ -Pyrazolyl Terpyridineplatinum(II) Dimer," *Acta Cryst.*, **1992**, *C48*, 1420.

15. J.-F. Roland and F. C. Anson, "Incorporation of Redox-Active Cations into Tungsten Oxide Coatings on Electrodes: Enhancement of Coating Stability and Electrocatalytic Activity," *J. Electroanal. Chem.*, **1992**, *336*, 245.

16. W. P. Schaefer, W. P. Connick, V. M. Miskowski and H. B. Gray, "A Bis(pyrazolyl)(bipyridyl) Platinum Complex," *Acta Cryst.*, **1992**, *C48*, 1776.

17. J. A. Bailey, V. M. Miskowski and H. B. Gray, "Spectroscopic and Structural Properties of Binuclear Platinum-Terpyridine Complexes," *Inorg. Chem.*, **1993**, *32*, 369.

18. J. A. Bailey, V. M. Miskowski and H. B. Gray, "A Diphenylformamidinate-Bridged Terpyridineplatinum(II) Dimer," *Acta Cryst.*, **1993**, *C49*, 793.

19. J. A. Labinger, A. M. Herring, D. K. Lyon, G. A. Luinstra, J. E. Bercaw, I. Horváth and K. Eller, "Oxidation of Hydrocarbons by Aqueous Platinum Salts: Mechanism and Selectivity," *Organometallics*, **1993**, *12*, 895.

20. G. A. Luinstra, J. A. Labinger and J. E. Bercaw, "Mechanism and Stereochemistry for Nucleophilic Attack at Carbon of Platinum(IV) Alkyls: Model Reactions for Hydrocarbon Oxidation with Aqueous Platinum Chlorides," *J. Am. Chem. Soc.*, **1993**, *115*, 3004.

21. E. P. Kelson, L. Henling, W. P. Schaefer, J. A. Labinger and J. E. Bercaw, "Electrocatalytic Oxidation by Binuclear Ruthenium Complexes Incorporating the Anionic Tripod Ligand $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}\{(\text{CH}_3\text{O})_2\text{P=O}\}_3]^-$," *Inorg. Chem.*, **1993**, *32*, 2863.

22. J. Zhang and F. C. Anson, "Coordination of Fe³⁺ by "Alizarin Complexone" Adsorbed on Graphite Electrodes to Produce Electrocatalysts for the Reduction of O₂ and H₂O₂," *J. Electroanal. Chem.*, **1993**, *353*, 265.

23. J. Zhang and F. C. Anson, "Electrocatalysts for the Reduction of O₂ and H₂O₂ Based on Complexes of Cu(II) with the Strongly Adsorbing 2,9-Dimethyl-1,10-Phenanthroline Ligand," *Electrochim. Acta*, **1993**, *38*, 2423.

24. C. Shi and F. C. Anson, "Electrocatalyst Coatings for Oxidations of Alcohols Based on Anodic Electrodeposition from Solutions of $\text{Ru}(\text{OH}_2)_6^{2+}$," *J. Electroanal. Chem.*, **1993**, 362, 273.
25. J. A. Bailey, V. J. Catalano and H. B. Gray, "A Monodentate 1,3-Diphenyltriazenido Terpyridineplatinum(II) Complex," *Acta Cryst.*, **1993**, C49, 1598.
26. J. A. Labinger, "Approaches to Catalytic Methane Conversion in Academic and Industrial Research: Comparison, Competition, Collaboration." *Química*, **1993**, 48, 25-7.
27. W. B. Connick and H. B. Gray, "(Bipyridyl)bis(iodo)platinum(II)," *Acta Cryst.*, **1994**, C50, 1040.
28. J. A. Labinger, J. E. Bercaw, G. A. Luinstra, D. K. Lyon and A. M. Herring, "Organometallic methane activation: Functionalization by aqueous platinum complexes." In *Natural Gas Conversion II: Proceedings of the Third International Gas Conversion Symposium, Sydney, July 4-9, 1993* (R. F. Howe and E. Curry-Hyde, Eds.), Elsevier, Amsterdam, **1994**, 515.
29. M. S. Freund, J. A. Labinger, N. S. Lewis and J. E. Bercaw, "Electrocatalytic Functionalization of Alkanes using Aqueous Platinum Salts." *J. Molec. Catal.*, **1994**, 87, L11.
30. G. A. Luinstra, L. Wang, S. S. Stahl, J. A. Labinger and J. E. Bercaw, "Oxidation of Zeise's Salt by $[\text{PtCl}_6]^{2-}$: A Mechanistic Model for Hydrocarbon Oxidation." *Organometallics* **1994**, 13, 755.
31. C. Y. Rong and F. C. Anson, "Simplified Preparations And Electrochemical-Behavior Of Two Chromium-Substituted Heteropolytungstate Anions." *Inorg. Chem.* **1994**, 33, 1064.
32. C. Shi and F. C. Anson, "Electrocatalysts for the Four-electron Reduction of O_2 and H_2O_2 Based on Adsorbed Cobalt Tetrapyrrolylporphyrin Molecules Linked by Aquaammine Complexes of Ruthenium(II)," *Inorg. Chim. Acta*, **1994**, 255, 215.
33. Y. Lei and F. C. Anson, "Mechanistic Aspects of the Electroreduction of Dioxygen as Catalyzed by Copper-Phenanthroline Complexes Adsorbed on Graphite Electrodes," *Inorg. Chem.*, **1994**, 33, 5003.
34. B. Steiger and F. C. Anson, "New Electrocatalysts for the Four-Electron Reduction of Dioxygen Based on (5,10,15-Tris(pentaammineruthenium(II)-(4-cyanophenyl)-20-(1-methylpyridinium-4-yl)porphyrinato)cobalt(II) Immobilized on Graphite Electrodes," *Inorg. Chem.*, **1994**, 33, 5767.
35. S. Surumpudi, S. R. Narayanan, E. Vamos, H. A. Frank, G. Halpert, A. LaConti, J. Josek, G. K. S. Prakash and G. A. Olah, "Advances in Direct Oxidation Methanol Fuel Cells." *J. Power Sources* **1994**, 47, 377.
36. J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer and H. B. Gray, "Electronic Spectroscopy of Chloro(terpyridine)platinum(II)." *Inorg. Chem.*, **1995**, 34, .
37. F. C. Anson, "Electrochemical Examples of Multiple-Electron Transfer," *Polymers for Advanced Technologies*, **1995**, 6, 112.
38. Y. Lei and F. C. Anson, "Dynamics of the Coordination Equilibria in Solutions Containing Cu(II), Cu(I) and 2,9-Dimethyl-1,10-Phenanthroline and Their Effect on the Reduction of O_2 by Cu(I)," *Inorg. Chem.*, **1995**, 34, 1083.

39. Y. Xie and F. C. Anson, "Analysis of the Cyclic Voltammetric Responses Exhibited by Electrodes Modified with Monolayers of Catalysts in the Absence and Presence of Substrates," *J. Electroanal. Chem.*, **1995**, *384*, 145.
40. C. Shi, B. Steiger and F. C. Anson, "Coordination Chemistry in Electrocatalysis," *Pure Appl. Chem.*, **1995**, *67*, 319.
41. B. Steiger and F. C. Anson, "Evidence of the Importance of Back-Bonding in Determining the Behavior of Ruthenated Cyanophenyl Cobalt Porphyrins as Electrocatalysts for the reduction of Dioxygen," *Inorg. Chem.*, **1995**, *34*, 3355.
42. G. A. Luinstra, L. Wang, S. S. Stahl, J. A. Labinger and J. E. Bercaw, "C-H Activation by Aqueous Platinum Complexes: A Mechanistic Study." *J. Organometal. Chem.*, in press.
43. "Formation and Reductive Elimination of a Hydridoalkylplatinum(IV) Intermediate upon Protonolysis of an Alkylplatinum(II) Complex." S. S. Stahl, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, in press.

Presentations (reports at ARPA/ONR project review meetings are not included):

1. S. R. Narayanan, S. Surumpudi, H. Frank, G. Halpert, R. Knieler, G. Stolp, G. K. S. Prakash and G. A. Olah, "Studies of the Electro-Oxidation of Methanol and Formaldehyde at Carbon-Supported Platinum and Platinum Alloy Electrodes," 182nd Electrochemical Society Meeting, Toronto, October 1992.
2. S. Surumpudi, S. R. Narayanan, H. Frank, E. Vamos, G. Halpert, A. Laconti, J. Kosec, G. K. S. Prakash and G. A. Olah, "Advances in Direct Oxidation Methanol Fuel Cell at Jet Propulsion Laboratory," SERT Conference, NASA Lewis Research Center, Cleveland, April 1993.
3. W. B. Connick, V. M. Miskowski, V. H. Houlding and H. B. Gray, "Spectroscopic Studies Of Linear-Chain Platinum(II)-Bipyridyl Complexes," 205th National Meeting of the American Chemical Society, Denver, March 1993.
4. J. A. Bailey, D. W. Low, V. M. Miskowski and H. B. Gray, "Spectroscopic Properties Of Some Mononuclear Platinum(II) Complexes," 205th National Meeting of the American Chemical Society, Denver, March 1993.
5. J. A. Labinger, J. E. Bercaw, G. Luinstra, D. K. Lyon and A. M. Herring, "Organometallic Methane Activation: Mechanism of C-H Functionalization by Aqueous Platinum Complexes," 13th North American Meeting of the Catalysis Society, Pittsburgh, May 1993.
6. C. Shi, B. Steiger and F. C. Anson, "Intramolecular Electron Transfer in Multi-Nuclear Electrocatalysts for the Reduction of O₂," 183rd Meeting of The Electrochemistry Society, Honolulu, May 1993.
7. J. A. Labinger, J. E. Bercaw, G. A. Luinstra, D. K. Lyon and A. M. Herring, "Organometallic methane activation: Functionalization by aqueous platinum complexes," Third International Gas Conversion Symposium, Sydney, Australia, July 1993.
8. S. S. Stahl, G. A. Luinstra, J. A. Labinger and J. E. Bercaw, "Methane Activation And Functionalization By Aqueous Platinum Complexes — A Mechanistic Investigation," 206th National Meeting of the American Chemical Society, Chicago, August 1993.

9. E. P. Kelson, J. A. Labinger and J. E. Bercaw, "Electrocatalytic Oxidation By Binuclear Ruthenium Complexes Incorporating the Anionic Tripod Ligand $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}((\text{CH}_3\text{O})_2\text{P}=\text{O})_3]^-$," 206th National Meeting of the American Chemical Society, Chicago, August 1993.
10. F. C. Anson, "New Multinuclear Dioxygen Reduction Catalysts," University of Paris, September 1993.
12. F. C. Anson, "Ruthenated Cobalt Porphyrins as Dioxygen Reduction Catalysts," Gordon Conference on Electrochemistry, January 1994.
12. J. A. Labinger, G. Luinstra, S. Stahl, L. Wang and J. E. Bercaw, "Mechanistic Studies On The Electrophilic Activation Of C-H Bonds By Aqueous Platinum Salts," 207th National Meeting of the American Chemical Society, San Diego, March 1994.
13. W. B. Connick, M. G. Hill and H. B. Gray, "Structure, Characterization And Photooxidation Of Platinum(II)-Bipyridyl Benzenedithiolate," 207th National Meeting of the American Chemical Society, San Diego, March 1994.
14. C. Shi, B. Steiger and F. C. Anson, "Coordination Chemistry in Electrocatalysis," XXX International Conference on Coordination Chemistry, Kyoto, Japan, July 1994.
15. J. A. Labinger, G. Luinstra, S. S. Stahl, L. Wang, J. H. Gilchrist and J. E. Bercaw, "Mechanism of Functionalization Of C-H Bonds By Platinum Salts In Aqueous Solution," 209th National Meeting of the American Chemical Society, Anaheim, April 1995.
16. S. S. Stahl, J. A. Labinger and J. E. Bercaw, "C-H Activation By Aqueous PtCl_4^{2-} : Mechanistic Insights from Model Chemistry," Gordon Conference on organometallic Chemistry, July 1995.
17. S. S. Stahl, J. A. Labinger and J. E. Bercaw, "C-H Activation By Aqueous PtCl_4^{2-} : Insights from Model Chemistry," 210th National Meeting of the American Chemical Society, Chicago, August 1995.

Patents Granted:

1. J. A. Labinger and E. Fowles, "Fuel Cells Based on Oxidation of Organics over Metal Exchanged β -Aluminas." US Patent 5,175,064, 29 December, 1992, assigned to California Institute of Technology.

Patents Filed:

1. S. Surumpudi, S. R. Narayanan, E. Vamos, H. A. Frank, G. Halpert, G. A. Olah and G. K. S. Prakash, "Organic Fuel Cell Methods and Apparatus." US Patent Application No. 08/135,007, 19 November, 1993.

Honors and Awards to Principal Investigators:

Fred C. Anson: Award in Electrochemistry, ACS Division of Analytical Chemistry., 1994

John E. Bercaw: Centennial Professorship of Chemistry, Caltech, 1993; 1992 Sir Edward Frankland Prize Lectureship, Royal Society of Chemistry; 1992 Distinguished Alumnus, School of Physical and Mathematical Sciences, North Carolina State University; Baker Lecturer, Cornell University, 1994.

Harry B. Gray: Priestley Medal of the American Chemical Society, 1991; Waterford Award of the Scripps Research Institute, 1992; Gibbs Medal of the Chicago Section, American Chemical Society, 1992; Linderstrøm-Lang Prize (Denmark), 1993; Honorary Doctorate of Science, University of Florence, 1993; Honorary Doctorate of Science, Columbia University, 1994.

Jay A. Labinger: Named Regional Editor for the US, *Journal of Molecular Catalysis*, 1994.

Nathan S. Lewis: ACS Award in Pure Chemistry, 1991; promotion to full Professor, Caltech, 1991.

George Olah: Tolman Award of the Southern California Section, American Chemical Society; Chemical Pioneer Award of the American Institute of Chemists, 1993; Honorary Doctorate of Science, University of Crete, 1994; Nobel Prize in Chemistry, 1994.

G. K. Surya Prakash: Promoted to Associate Professor with tenure, USC, 1993; promoted to Full Professor, 1994.

Part IV: Transitions

The patent for organic fuel cells (see Patents Filed, above) has been licensed for commercial development by DTI and DCT International.

Summaries of Highlighted Publications/Presentations:

Publication #9 (C. Shi and F. C. Anson, "Multiple Intramolecular Electron-Transfer in the Catalysis of the Reduction of Dioxygen by Cobalt *meso*-Tetrakis(4-pyridyl)porphyrin to Which Four Ru(NH₃)₅ Groups Are Coordinated," *J. Am. Chem. Soc.*, **1991**, *113*, 9564) reports the success of a strategy for direct four-electron reduction of O₂ at an electrode. By attaching redox-active metal centers to a dioxygen-activating cobalt porphyrin complex and binding the entire assembly in a Nafion coating on the electrode surface, efficient electroreduction of O₂ directly to H₂O was achieved. This demonstrates a promising approach to improving cathode performance in fuel cells.

Publication #21 (E. P. Kelson, L. Henling, W. P. Schaefer, J. A. Labinger and J. E. Bercaw, "Electrocatalytic Oxidation by Binuclear Ruthenium Complexes Incorporating the Anionic Tripod Ligand [(η⁵-C₅H₅)Co{(CH₃O)₂P=O}₃]⁻," *Inorg. Chem.*, **1993**, *32*, 2863) reports electrooxidation of formaldehyde at low potentials by a designed soluble ruthenium complex in solution or attached to an electrode. This validates the premise that soluble catalysts may offer advantages over traditional metal surfaces for efficient electrooxidation of organic substrates under conditions suitable for direct fuel cell applications.

Publication #35 (S. Surumpudi, S. R. Narayanan, E. Vamos, H. A. Frank, G. Halpert, A. LaConti, J. Josek, G. K. S. Prakash and G. A. Olah, "Advances in Direct Oxidation Methanol Fuel Cells." *J. Power Sources* **1994**, *47*, 377) describes an advanced liquid feed aqueous methanol fuel cell apparatus that resulted from this project, and points out its potential practical applications.

Presentation #7 (J. A. Labinger, J. E. Bercaw, G. A. Luinstra, D. K. Lyon and A. M. Herring, "Organometallic methane activation: Functionalization by aqueous platinum complexes," Third International Gas Conversion Symposium, Sydney, Australia, July 1993) emphasizes the value of mechanistic study in delineating the special role of soluble catalysts in activation of methane and other organic compounds and their potential applications in practical schemes.